Short Communication

A CONTRIBUTION TO SEMENOV'S GENERAL THEORY OF THERMAL IGNITION REGARDING THERMAL ANALYSIS

V. M. GORBACHEV

Institute of Inorganic Chemistry, Siberian Department of the Academy of Sciences of the USSR, Novosibirsk, USSR

(Received April 27, 1981)

The general theory of thermal ignition under the conditions of thermal analysis of flammable substances is discussed. For a linear heating rate of the specimen the ignition temperature is obtained from the relationship

$$(\mathrm{d}T/\mathrm{d}t)_b - \frac{q}{(\mathrm{d}T/\mathrm{d}t)_b} = \frac{E}{RT_b^2}(T_b - T_c')$$

where T_c' is the temperature of the reactor wall (heated at the rate q) at the starting moment of the development of the thermal explosion.

It is well known that when an exothermic reaction takes place in an insulated space and the heat liberated in the reaction is higher than the heat transmitted to the environmental medium, this leads to the self-heating of the reaction system and to a further increase of the rate of reaction, which will finally result in a non-steady-state, accelerating combustion of the substance. This phenomenon was termed "thermal explosion" and studied from both theoretical and applied aspects by Semenov [1] and his school.

However, the complex mathematical apparatus of the modern theory of thermal explosion [2, 3] under the conditions of normal routine thermal analysis cannot always be employed by thermoanalysts. For this reason, a uniformization of the general theory of thermal explosion for the above purposes would in our opinion be useful.

In its mathematical form, the condition of ignition formulated by Semenov is the equality of heat liberation Q_1 and heat transmission Q_2:

$$Q_1 = Q_2 \tag{1}$$

$$\frac{\mathrm{d}Q_1}{\mathrm{d}T} = \frac{\mathrm{d}Q_2}{\mathrm{d}T}. \tag{2}$$

In general, the temperature of ignition will depend on the nature of the flammable substance, its concentration in the mixture, the material of the wall of the reactor and its geometry, the nature of the environmental medium and other factors affecting the thermal regime of the process. Consequently, an exact determination of the thermal ignition temperature under the conditions of programmed heating of the substance is not possible but it can be approximated to on the basis of the classical theory of thermal explosion of Semenov [1] and the means of performace of the thermoanalytical experiment.

The rate of the chemical reaction may be expressed from the data of non-isothermal kinetics, using the standard symbols, as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-E/RT\right) f(\alpha) \tag{3}$$

where α is the conversion or the degree of combustion, and $f(\alpha)$ is a characteristic function of the concentration and topochemistry of the transformation. In the general case, $f(\alpha) = (1 - \alpha)^n$. However since, ignition starts in the range of low combustion degrees, $(1 - \alpha)^n \to 1$ and Eq. (3) will be simplified to the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-E/RT\right). \tag{4}$$

Hence, the corresponding heat Q_1 liberated within the reactor will be

$$Q_1 = \bar{Q} A \exp\left(-E/RT\right) \tag{5}$$

where $\bar{Q}$ is the thermal effect of the chemical reaction (kcal/mol or kJ/mol). The amount of heat transferred by the wall of the reactor to the surrounding medium is

$$Q_2 = \beta S(T_b - T_c) = L(T_b - T_c) \tag{6}$$

where β is the overall heat transmission coefficient, S is the external surface of the reactor and T_c is the temperature of the wall of the reactor and of the furnace space programmed according to the linear relationship $T_c = T_0 + qt$. Taking Eq. (2) into account, we obtain

$$\bar{Q} A \exp\left(-E/RT\right) \frac{E}{RT_b^2} \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b = L\left[\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b - q\right]. \tag{7}$$

By combining Eqs (6) and (7), one finally obtains

$$\Theta = \frac{(\mathrm{d}T/\mathrm{d}t)_b - q}{(\mathrm{d}T/\mathrm{d}t)_b} = \frac{E}{RT_b^2}(T_b - T_c') \tag{8}$$

where T_c' is the temperature of the reactor wall and the furnace environment according to the heating program, at the moment when the thermal explosion starts. This temperature can be read off the thermoanalytical curve. Considering the essential concept of the thermal explosion, the value $\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_b$ at the moment of the explosion will be substantially higher than q at moderate heating rates of the reaction system, and in this case $\Theta \approx 1$. However, if the small value is taken into account, then

$$E/RT_b^2(T_b - T_c') < 1\,. \tag{9}$$

According to Semenov's theory [1], at a constant temperature of the medium T.

$$E/RT_b^2(T_b - T_0) = 1\,. \tag{10}$$

By solving inequality (9) one obtains

$$ET_c' > (E - RT_b)T_b\,. \tag{11}$$

By substituting the value RT_b in the brackets by RT_c', which is close to its value, inequality (11) will assume the form

$$ET_c' \simeq (E - RT_c')T_b \tag{12}$$

or

$$T_b = \frac{ET_c'}{E - RT_c'}\,. \tag{13}$$

According to Semenov, the temperature of self-ignition is usually below 1000 K and the activation energy is usually higher than 84 kJ/mol. By way of example, let us assume the values $T_c' = 700$ K and $E = 125$ kJ/mol. Computation *via* Eq. (13) yields the value $T_b = 734$ K. According to Semenov's theory (Eq. 10) the ignition temperature T_b is 735 K (at $T_0 = 700$ K).

If the thermoanalytical curves allow a qualitative identification of the values Θ, T_c and T_b, the activation energy E may be estimated from these values.

References

1. N. N. SEMENOV, O nekotorykh problemakh khimicheskoy kinetiki i reaktsionnoy sposobnosti (On some problems of chemical kinetics and reactivity). Izd. AN SSSR, Moscow, 1958, p. 421.
2. A. G. MERZHANOV and F. I. DUBOVITSKY, Sovremennoe sostoyanie teorii teplovogo vzryva (Current state of the theory of thermal explosion). Uspekhi khimmi, 35 (1966) 656.
3. A. G. MERZHANOV, Combustion and Flame, 11 (1967) 201.